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THE LONG-TERM CORROSION TEST FACILITY AT LAWRENCE LIVERMORE NATIONAL LABORATORY

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ABSTRACT

The long-term corrosion test facility (LTCTF) at the Lawrence Livermore National Laboratory (LLNL) consisted of 22 vessels that housed more than 7,000 corrosion test specimens from carbon steels to highly corrosion resistant materials such Alloy 22 and Ti Grade 7. The specimens from LTCTF range from standard weight-loss coupons to U-bend specimens for testing susceptibility to environmentally assisted cracking. Each vessel contained approximately 1000 liters of concentrated brines at 60°C or 90°C. The LTCTF started its operations in late 1996. The thousands of specimens from the LTCTF were removed in August-September 2006. The specimens are being catalogued and stored for future characterization. Previously removed specimens (e.g. 1 and 5 years) are also archived for further studies.

Keywords: Long-term corrosion test facility, weight loss, crevice, U-bend, simulated concentrated ground waters

INTRODUCTION

The Yucca Mountain Project (YMP) is currently preparing a license application for the nation's first-ever repository for spent nuclear fuel and high-level radioactive waste [1]. For more than two decades, the Project conducted an extensive scientific effort to determine whether Yucca Mountain, Nevada is a suitable site for a deep underground facility called a repository [1]. The purpose of a repository is to safely isolate highly radioactive nuclear waste. On July 9, 2002, the U.S. Senate cast the final legislative vote approving the development of a repository at Yucca Mountain. Current plans call for submitting an application to obtain a license from the U.S. Nuclear Regulatory Commission no later than June 30, 2008 [1].

Yucca Mountain is located on federal land in a remote area of Nye County in southern Nevada, about 100 miles northwest of Las Vegas, Nevada. The proposed Yucca Mountain repository withdrawal area would occupy about 230 square miles (150,000 acres) of federal land that is currently under the control of the U.S. Department of Energy, the U.S. Air Force, and the Bureau of Land Management. Yucca Mountain is a ridge comprised of layers of volcanic rock, called "tuff." This rock is made of ash that was deposited by successive eruptions from nearby volcanoes, between 11 and 14 million years ago. These volcanoes have been extinct for millions of years. Yucca Mountain receives less than 7.5 inches (191 mm) of precipitation on average per year [1].

With its desert climate, deep water table, and thick layers of stable rock, Yucca Mountain provides an excellent geologic setting for a repository. Even though the geologic site is stable, it is planned to complement the many natural features with additional engineered barriers. The repository design includes a series of emplacement tunnels excavated deep underground in solid rock. The layout and attributes of these tunnels are engineered to manage the heat that would be generated by the waste. The engineered features, which include waste packages, drip shields, and tunnel inverts, will be within the emplacement tunnels [1]. The repository design allows for future generations to choose whether to close and seal the repository or to keep it open and monitor it for up to 300 years before making decisions to decommission and close the facility. If while the repository is open, future technologies provide a better disposal solution or a use for the nuclear materials, the design allows for the waste to be removed from the repository [1].

The proposed engineered barriers that will retard the release of radioactive material will consist of a sealed waste package and a detached drip shield. The waste package will be double walled with an inner shell of a type 316 stainless steel (with modified carbon and nitrogen compositional ranges) and an outer barrier of Alloy 22 (N06022). The 316 SS shell in the waste package will serve to shield radiation and also provide mechanical integrity. The primary purpose of the outer wall of the container Alloy 22 is to provide protection against corrosion. Alloy 22 (N06022) was selected for the corrosion resistant barrier of the waste packages because it is well known commercially for its excellent corrosion behavior in aggressive environments [2-4]. Because of its high Cr content, Alloy 22 remains passive in most industrial environments and thus, has an exceptionally low general corrosion rate. The drip shield will be made with Titanium Grade 7 (R52400) and a high strength Ti alloy (Ti Gr 29 or R56404). Welding between Ti Gr 7 and Ti Gr 29 will be done using Ti Gr 28 (R56323). The presence of the drip shield will guard the waste packages against water seepage and rock fall from the drift walls [2-4].

Table 1. Waters Compositions (mg/L)

Ion	SDW pH 10	SCW pH 8-10	SAW pH 2.8	SCMW pH 7.8	J-13 Well pH 7.4
K^+	34	3400	3400	309	5.04
Na^+	409	40,900	37,690	14	45.8
Mg^{2+}	1	< 1	1000	0.3	2.01
Ca^{2+}	0.5	< 1	1000	197.5	13
F^-	14	1400	0	1.3	2.18
Cl^-	67	6700	24,250	4.3	7.14
NO_3^-	64	6400	23,000	5.2	8.78
SO_4^{2-}	167	16,700	38,600	864.7	18.4
HCO_3^-	947	70,000	0	6.4	128.9
SiO_2 (aq)	~ 40	~ 40	~ 40	22.7	61.1

THE ENVIRONMENT

Waters that may contact the waste packages are expected to be in the form of multi-ionic concentrated aqueous solutions. These solutions may form via two mechanisms: (1) Dripping from the drift wall (in the absence of the drip shield) and concentrating on the waste package surface, or (2) Deliquescence of salts that may accumulate on top of the waste package during dry periods. The ground waters that are associated with the Yucca Mountain region contain small amounts of chloride but also nitrate, sulfate and carbonate [2,4]. Table 1 shows the composition of water from the saturated zone from a well designated, J-13 near the repository site [5]. Table 1 also shows the composition of various laboratory-prepared, aqueous, concentrated electrolyte solutions in which testing was performed. These electrolyte solutions ranged from pH 2.8 to 10 and were designated as simulated acidified water (SAW), simulated concentrated water (SCW), simulated dilute water (SDW), and simulated cement modified water (SCMW).

MATERIALS CHARACTERIZATION

The Yucca Mountain Project (YMP) is supported by scientific research in several national laboratories including Lawrence Berkeley, Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory, Sandia National Laboratories and the U.S. Geological Survey. Each laboratory is specialized in different areas of the Project. LLNL has historically been the primary site for corrosion testing, phase stability and metallurgical studies and other material characterization research. Corrosion studies included the corrosion testing of thousand of specimens in the long-term corrosion test facility (LTCTF). Other corrosion studies included the testing of Alloy 22 and titanium alloys for resistance to localized corrosion and the determination of the localized corrosion repassivation potential using mainly electrochemical techniques.

THE LONG TERM CORROSION TEST FACILITY

The Long-Term Corrosion Test Facility (LTCTF) started its operations in 1996 to provide corrosion engineering data on a variety of candidate materials for fabrication of nuclear waste packages for the Yucca Mountain Project. The facility was designed to allow a comprehensive evaluation of all the forms of corrosion and to permit successive withdrawals of test specimens to obtain corrosion rates and behavior over different time intervals. Several specimen configurations were used for evaluating different forms of corrosion: general corrosion, crevice corrosion, pitting corrosion, stress corrosion cracking, etc. Since the operation of the LTCTF started in 1996 the materials selection for the repository evolved. At one time the YMP considered the use of a corrosion allowance material for the outer shell of the waste package and a corrosion resistant material for the inner shell [4].

The LTCTF initially included 28 large polymeric vessels containing six different waters at different temperatures that were prepared to simulate the bounding chemical and thermal conditions in the repository. More than 20,000 specimens were exposed in the vessels during the decade long experiment. Specimens had been periodically withdrawn at intermediate times to monitor the corrosion behavior of the different alloys as a function of time. The partial withdrawal of specimens was generally for selected materials, such as Alloy 22 and Ti Gr 7.

Partial specimen withdrawals occurred for example at 1 year, 2-year and 5+-year exposure. Results for the intermediate withdrawals have been published before [6-9].

Materials tested in the LTCTF included corrosion allowance materials (e.g. carbon steels, alloy steels), intermediate corrosion resistant alloys (copper-based) and corrosion resistant alloys (nickel and titanium alloys) [11]. The tested specimens were welded and non-welded.

Each vessel in the LTCTF contained up to six racks with specimens. In most of the vessels the racks started testing at different times. For example, in Vessels 25-30 the testing of the racks containing nickel alloys and Ti Gr 12 and Ti Gr 16 started in early 1997 while the racks containing the specimens of Ti Gr 7 started in December 1999.

Figure 1 shows a schematic of one vessel from the LTCTF. There were six ports at the top of each vessel for the racks that contained the coupons. Figure 2 shows the vessels side by side during the operation of the LTCTF and Figure 3 shows the post-test appearance of one of the racks. Each rack could have contained up to 246 specimens.

The volume of each vessel was approximately 2,000 L and they were filled with 1,000 L of electrolyte solution. That is, the specimens in the top part of the rack (Figure 3) were exposed to the vapor phase and the specimens in the lower part of the rack were exposed to the liquid phase of the electrolyte. A few specimens in the middle of the rack were exposed to the waterline. The specimens were exposed to the free corrosion potential in the aerated vessels. The corrosion potential (E_{corr}) was not monitored during the tests.

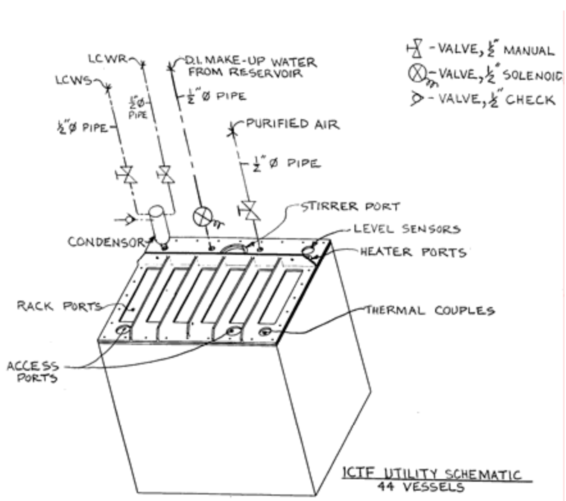

Figure 1. Schematic of one vessel from the LTCTF

Figure 2. Side by side vessels during the operation of the LTCTF

Figure 3. Typical rack in each vessel showing various type of specimens

Table 2 shows the summary of the 22 vessels that were in operation at the time of the final shut down of the LTCTF in August-September 2006. Table 2 also shows the type of solution and temperature in each vessel as well as the starting time and the shut down time. Different racks in each vessel may have had different exposure times. Only the time for the longest exposure rack is shown in Table 2.

Table 2 shows that all the vessels in the LTCTF were in operation for times longer than approximately 3200 days (8.8 years). The longest exposure rack was in Vessel 23 with 3555 days (9.7 years). Vessels 25-30 (shadowed in Table 2) housed the specimens for Alloy 22 and Ti Gr 7. The longest exposure time was for Vessel 25 with 3445 days (9.4 years) and the shortest was for Vessel 30 with 3380 days (9.3 years).

Table 2. Vessels from LTCTF Dismantled in 2006

Vessel	Solution	T, °C	Start Date	Shut Down Date	Exposure time, days
9	SCW	60	25Sep97	25Aug06	3210
10	SCW	90	25Sep97	25Aug06	3210
11	SCW	60	25Sep97	18Aug06	3203
12	SCW	90	25Sep97	22Aug06	3207
13	SDW	60	24Sep97	21Aug06	3207
14	SDW	90	24Sep97	24Aug06	3210
17	SDW	60	15Sep97	29Aug06	3224
20	SCW	90	15Nov96	14Aug06	3509
21	SCW	60	28Oct96	08Aug06	3520
22	SDW	90	10Oct96	15Aug06	3545
23	SDW	60	24Sep96	09Aug06	3555
24	SDW	90	18Sep97	29Aug06	3221
25	SAW	60	06Feb97	01Sep06	3445
26	SAW	90	21Feb97	06Sep06	3435
27	SCW	60	10Mar97	01Sep06	3411
28	SCW	90	10Apr97	01Sep06	3381
29	SDW	60	14Apr97	06Sep06	3382
30	SDW	90	17Apr97	07Sep06	3380
31	SCMW	60	17Sep97	31Aug06	3224
32	SCMW	90	18Sep97	31Aug06	3223
33	SCMW	60	22Sep97	11Aug06	3199
34	SCMW	90	22Sep97	17Aug06	3205

Alloys

Table 3 shows the alloys that were tested in the LTCTF. They ranged from carbon steel to the highly corrosion resistant Alloy 22 and Ti Gr 7

Table 3. Alloys tested in the LTCTF

Alloy, ASTM, UNS	Prefix	Nominal Composition (wt%)	Specimens Tested in Vessels
825, B 424, N08825	A	~30Fe-42Ni-22Cr-3Mo-2Cu-1Ti	9-10, 17, 24, 25-30, 31, 32
G-3, B 582, N06985	B	~40Ni-22Cr-20Fe-7Mo-2Cu	25-30
C-4, B 575, N06455	C	~68Ni-16Cr-16Mo	25-30
C-22, B 575, N06022	D	~58Ni-22Cr-13Mo-3W-4Fe	9-10, 17, 24, 25-30, 31-32
Ti Gr 12, B 265, R53400	E	~98Ti-0.8Ni-0.3Mo	9-10, 17, 24, 25-30, 31-32
Ti Gr 16, B 265, R52402	F	~99Ti-0.06Pd	25-30
400, B 127, N04400	G	~33Cu-67Ni	11-14
CDA715, B 171, C71500	H	70Cu-30Ni	11-14
Alloy Steel, A387 Gr 22, K21590	I	~99Fe-2.25Cr-1Mo	9-10, 17, 20-24, 31-34
Carbon Steel A516 Gr 55, K01800	J	~99Fe-0.8Mn-0.3Si	9-10, 17, 20-24, 31-34
Cast Steel A27 Gr 70-40, J02501	K	~98Fe-0.25C max-1.2Mn max	20-23, 33-34
625, B 443, N06625	L	~58Ni-21Cr-9Mo-3.5(Cb+Ta)	9-10, 17, 24, 25-30, 31-32
686, B 575, N06686	M	~58Ni-21Cr-16Mo-4W	9-10, 17, 24, 31-32
Ti Gr 7, B 265, R52400	N	~99Ti-0.18Pd	25-30

The specimens were segregated in vessels according to their corrosion resistance. Vessels 25-30 contained the corrosion resistant alloys currently specified for the outer barrier of the waste package (Alloy 22) and for the drip shield (Ti Gr 7).

Specimens

Several types of specimens for each type of alloy were used for testing. The specimens included: (1) For general corrosion by weight-loss, a 1-inch x 2-inch x 0.125-inch coupon, (2) For crevice corrosion susceptibility, a 2-inch x 2-inch x 0.125-inch coupon containing an inert crevice former made of PTFE material, (3) For stress corrosion cracking susceptibility, a U-bend specimen and, (4) For galvanic corrosion susceptibility, corrosion resistant coupons were sandwiched -for full electrical contact- with corrosion allowance coupons (different combinations of surface area between the two type of materials was used).

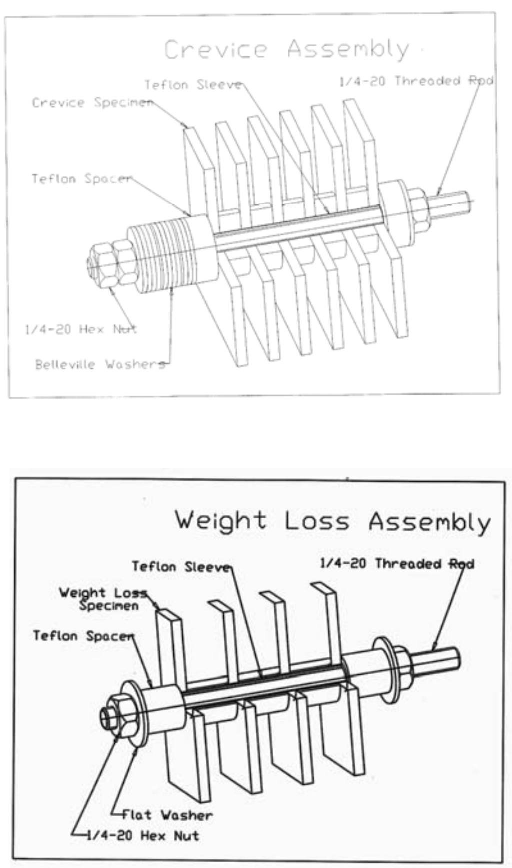

Figure 4. Specimen assembly for crevice corrosion susceptibility and weight-loss

Figure 5. Ti Gr 7 U-Bend specimen tested for 6.6 year in SAW at 60°C. No Cracking

Figure 6. Alloy 22 U-Bend specimen tested for 9.3 years in SCW at 90°C. No cracking

Figure 7. Alloy 22 creviced specimen tested for 9.3 years in SCW at 90°C. No crevice corrosion

Figure 4 shows the schematic of the crevice corrosion susceptibility and weight loss specimen assembly (one fourth of the specimens is showed "carved out" to illustrate the attaching mechanism to the holding rod). Each assembly contained six coupons of each alloy (3 welded and 3 non-welded). They were attached horizontally from the test rack (Figure 3).

Figure 5 shows a Ti Gr 7 welded U-bend specimen (NUE019) removed from Rack 1 in Vessel 25 after 2411 days of exposure in the liquid phase of SAW solution at 60°C. The specimen was free from environmental cracking. Figure 6 shows an Alloy 22 welded U-bend specimen (DUB120) removed from Rack 5 in Vessel 28 after 3381 days of exposure in the liquid phase of SCW solution at 90°C. The specimen was free from environmental cracking.

Figure 7 shows an Alloy 22 welded creviced specimen (DCB119) removed from Rack 5 in Vessel 28 after 3381 days of exposure in the liquid phase of SCW solution at 90°C. Even though the specimen still needs to be cleaned, it is apparent that it was free from crevice corrosion and the weld seam was not etched.

Future Studies

The remaining specimens from the LTCTF are in storage at LLNL for future evaluation. The first specimens that will be studied will include Alloy 22 and Ti Gr 7. Alloy 22 specimens have been exposed to the electrolytes for over 9 years and Ti Gr 7 for over 6 years. Current evaluations include the visual observation and imaging of the specimens individually, both optically and using a scanning electron microscope. The flat coupons (weight loss and creviced) will be cleaned for weight loss determination in the three electrolyte solutions at the two exposed temperatures. Other studies will include the surface analyses such as studies on the thickness and composition of the passive film formed on the different materials. Studies of the U-bend specimens will determine the relative susceptibility of the different alloys to environmentally assisted cracking and the effect of welding on the cracking resistance. From the galvanic specimens it will be important to determine the effect of galvanic coupling on the hydrogen uptake of the titanium alloys.

In storage at LLNL are also specimens removed in 2002 and in previous years. A detailed study of these specimens (especially for the corrosion resistant alloys) may yield information on the effect of testing time on the persistence and nature of the passive film that forms on the different materials.

SUMMARY AND CONCLUSIONS

- The Long-Term Corrosion Test Facility (LTCTF) operated at Lawrence Livermore National Laboratory (LLNL) for more than 9 years
- More than twenty thousand specimens of fourteen (14) different alloys have been tested in the LTCTF.
- Specimens exposed to several types of environments included coupons for weight loss as well as U-bend for environmental cracking susceptibility
- The majority of the specimens removed from the LTCTF still need to be analyzed

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